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Levels and Chiral Signatures of Organochlorine Pesticides in Urban Soils of Yinchuan, China

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Abstract In this study, residual level and enantiomeric composition of typical organochlorine pesticides (OCPs) were surveyed in urban soils of Yinchuan, China. The median levels of $\sum$HCHs and $\sum$DDTs were 0.852 and 2.24 ng/g, respectively, which suggested little risk for ecological environment and human health in the study area. Both chiral α-HCH and *o,p′*-DDT displayed the non-racemic signatures in all samples. The isomer ratios of $\sum$HCHs and $\sum$DDTs combined with enantiomer fractions (EFs) of α-HCH and *o,p′*-DDT, suggested that contamination source of HCHs derived from historical HCHs (including technical HCHs and Lindane) and that of DDTs originated from old source with the usage of mixed technical DDTs and dicofol.

Keywords Survey · Enantiomeric composition · HCHs · DDTs

Organochlorine pesticides (OCPs) have been widely used for several decades. In the light of the fact that their persistence in nature and negative impacts on human and other organisms, the application of OCPs was banned in China for more than 20 years. However, residues of OCPs in the environment are still detectable. Some organochlorine pesticides are chiral, such as trans-chlordane (TC), cis-chlordane (CC), heptachlor, α-HCH and *o,p′*-DDT, and they were usually used by racemic mixture. To our knowledge, most of previous investigations commonly focused on the total residual levels, as a result, current knowledge of them was often inaccurate due to the different toxicological properties and rates of metabolism of chiral pesticides in the environment (Muller and Kohler 2004; Wiberg et al. 2001). Therefore, study on chiral signatures of pollutants will be helpful to further understand the toxicological mechanism and environmental behavior. Accordingly, it has been proved that chiral signatures of compounds would provide useful and complementary information for distinguishing "new" source from "old" sources (Shen et al. 2004), enantimeric analysis have received more and more attention along with the development of chiral analysis technology. The enantiomeric composition can be expressed as enantiomer fractions (EFs) (Harner et al. 2000), defined as $A_+/(A_+ + A_-)$, where A_+ and A_- correspond to the peak areas of the (+) and (−) enantiomers. If pesticide is racemic and no metabolism has occurred, the EFs should be 0.500, whereas preferential degradation of the (+) or (−) enantiomer (EFs < 0.500 or EFs > 0.500).

Until now, there have been numerous studies of chiral OCPs in agricultural soils (Wiberg et al. 2001; Li et al. 2006; Fakconer et al. 1997; Leone et al. 2001), but there are very few reports in urban soils. Because of intense influence of industry, trade, traffic, human activity and so on, organic pollutants in urban soil not only have various species but high residual levels, in addition, the urban population is crowded, so the citizens health would be faced with potential threat. The aim of this work was to analyze OCPs pollutant sources and evaluate ecological risk in urban soils of Yinchuan city, China. Yinchuan is

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capital of Ningxia Hui Autonomous Region, and locates on upstream of Yellow River and middle of Ningxia plain. Region scope is in north latitude 37°29′–38°53′, east longitude105°49′–106°53′. At present, Yinchuan urban district area is 1,482 square kilometers, including three districts (Xingqing, Jinfeng and Xixia).

Materials and Methods

Stock solutions of seven organochlorine pesticides including *α*-, *β*-, *γ*-HCH, *p,p*′-DDT, *p,p*′-DDE, *o,p*′-DDT and *p,p*′-DDD were purchased from the National Research Center for Certified Reference Materials of China at concentration of 100.0 mg/L. 2,4,5,6-Tetrachloro-*m*-xylene (TCMX) as a surrogate standard was purchased from Supelco (Bellefonte, USA). The solutions were further diluted with isooctane to prepare working standards. Anhydrous sodium sulfate (analytical grade, Qingdao ocean chemical plant, China) was pretreated in a muffle furnace at 600°C for 6 h. Sulfuric acid silica gel (50% w/w concentrated sulfuric acid) was prepared by drop wise addition of concentrated H_2SO_4 (analytical grade, Beijing chemistry reagent factory, China) to dry silica gel (100–200 mesh) under continuous stirring with an electromagnetic stirrer. Hexane (pesticide grade, J. T. Baker, USA) was used. Acetone (analytical grade, Beijing chemistry reagent factory, China) was redistilled in all-glass systems to remove impurities prior to use.

Twelve surface soil samples (0–5 cm) consisting of eight park soils (BT, ZS, BH, MC, SL, YH, XX and SH), two green land soils (G1 and G2) and two suburb farmland soils (F1 and F2) were collected in three districts of Yinchuan city, which was seen in Fig. 1. The soil samples were carried to lab, then were freeze-dried, thoroughly mixed and sieved to 40 mesh, wrapped by pre-cleaned aluminum foil and maintained at 4°C refrigerator until further processing.

About 10 g of soil was ground with anhydrous sodium sulfate into free flowing powder. The sample was ultrasonically extracted in centrifuge tube with 30 mL of 1:1 acetone:hexane (V:V) for 5 min and then the extract was separated by centrifugation. The process was repeated three times. The solvents were combined and added activated copper to remove sulfur, and then solvents were concentrated to 1–2 mL by using a rotary evaporator. The concentrated extracts were cleaned by passing through columns packed with 8 g sulfuric acid silica gel (50%, w/w) that was capped with 2 g of anhydrous sodium sulfate. The column was eluted with 50 mL hexane. The eluent was collected and reduced to 0.2 mL. The fraction was further carried out by using an LC–Si column (sorbent mass 500 mg, volume 3 mL, Supelco Park Bellefonate, PA 16823-0048, USA). After the column was conditioned with 5 mL hexane, the sample was loaded on the column and then eluted with 10 mL hexane. The sample solution was collected and concentrated to 0.1 mL by using a gentle steam of nitrogen for following GC/ECD determination.

Quantification of OCPs was carried out with an Agilent 6890 gas chromatography equipped with a micro-cell ^{63}Ni electron capture detector (*μ*-ECD). The separation was performed on a DB-5 fused silica capillary column (30 m × 0.25 mm i.d., and 0.25 μm film thickness). The carrier gas was nitrogen with a flow of 0.7 mL/min. The

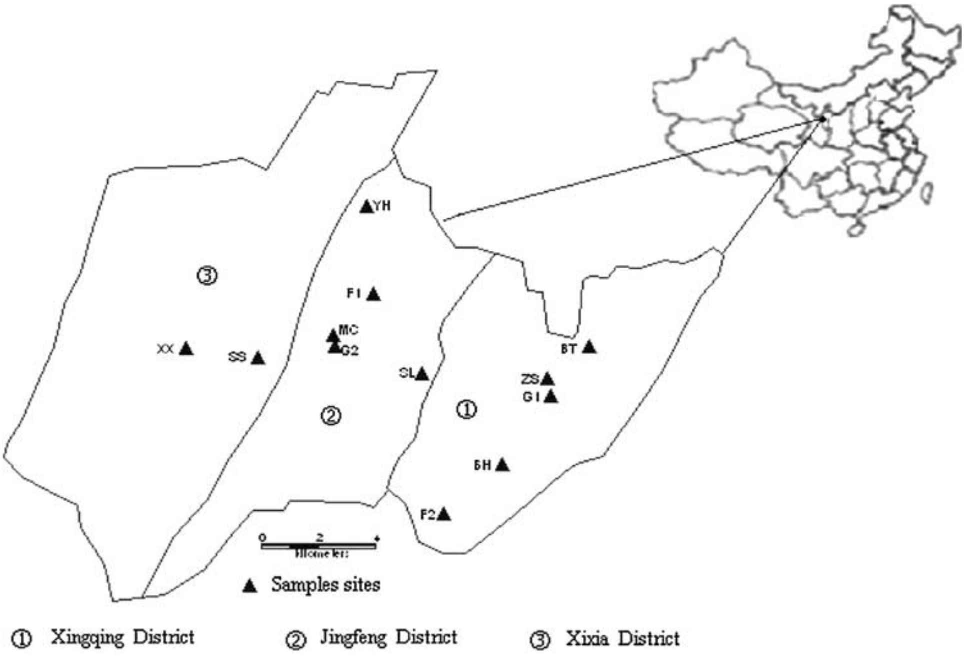

Fig. 1 The sampling layout of Yinchuan city

injector and detector temperatures were 225°C and 300°C, respectively. Samples (1.0 µL) were injected manually in splitless mode at 100°C, held for 2 min, increased to 160°C at 10°C/min, then increased to 230°C at 4°C/min, held for 5 min, followed by a 10°C/min ascent to 280°C, which was maintained for 10 min. To confirm the results, selected typical samples were checked with a Hewlett–Parkard 6890-5973MSD system. The GC-MS parameters were the same as described above. The mass spectrometer was operated in electron impact ionization mode with the electron energy of 70 eV. Target compounds were monitored with selected ion monitoring mode (SIM).

Determination of EFs of α-HCH and *o,p*′-DDT was done by an Agilent 6890 gas chromatography equipped with a micro-cell ^{63}Ni electron capture detector (*µ*-ECD). The enantiomer separation was performed on BGB-172 chiral column (30 m × 0.25 mm i.d., 0.25 µm film thickness). The carrier gas was nitrogen with a flow of 0.7 mL/min. The injector and detector temperatures were 250°C and 300°C, respectively. Samples (2 µL) were injected splitless (split opened after 1.5 min) at 90°C, held for 1 min, 15°C/min to 140°C, 2°C/min to 210°C, held for 5 min, 20°C/min to 240°C, held for 10 min. The elution orders for α-HCH and *o,p*′-DDT were determined from previously published work using the same column type (Fakconer et al. 1997; Ridal 1997; Wiberg et al. 2001).

A solvent blank sample followed the sample to be analyzed through the entire analysis procedure. No contaminants of OCPs were found in the solvent blanks (n = 3). Prior to extraction, each of the soil samples was spiked with a known amount of TCMX as a surrogate. The average recovery of the TCMX surrogate was above 84.0%. The average recoveries of OCPs were done by spiking standards in a matrix blank. The average recoveries of OCPs were in the range of 87–95%, and RSD was 3.20%–7.10% (n = 5). The limits of detection (LODs) were taken as three times the response of the signal-to-noise (S/N), and ranged from 0.010 to 0.140 µg/kg. For a satisfactory enantiomeric analysis, racemic standard solutions at concentration of 200 µg/L were repeatedly injected seven times to check the individual enantiomer response during the analysis, and mean EF of α-HCH and *o,p*′-DDT were 0.500 ± 0.002, 0.501 ± 0.001, respectively. And RSD (relative standard deviation) of seven time analysis were 0.6% for α-HCH, 1.3% for *o,p*′-DDT. This reproducibility allows determination of enantiomer ratio changes of even a few percent with sufficient significance.

Results and Discussion

All of the samples contained residues of OCPs, the residual levels in soils are summarized in Table 1. After preliminary distributed type examination, discovered various data present the non-normal distribution, therefore the median value replaced the mean value in the following data discussion.

Table 1 The residual levels (µg/kg, dry weight) of seven OCPs in urban soils of Yinchuan city, China

Pesticide	Minimum	Maximum	Mean	RSD (%)	Median
α-HCH	0.382	0.0172	0.120	109	0.0630
β-HCH	0.261	73.4	7.65	274	0.558
γ-HCH	0.0523	0.459	0.210	63.1	0.204
p,p′-DDE	0.135	523	45.2	332	1.10
p,p′-DDD	0.0127	23.8	2.08	329	0.0780
o,p′-DDT	0.0700	22.9	2.47	263	0.338
p,p′-DDT	0.0462	499	42.3	339	0.500
∑HCHs	0.306	74.2	7.98	265	0.852
∑DDTs	0.410	1,068	92.1	334	2.24

For HCHs, the residual level of ΣHCHs (equivalent sum of α-, β- and γ-HCH) ranged from 0.391 to 74.2 µg/kg, the median was 0.852 µg/kg. The levels of HCHs in the most soils were in the range of those in background soils in China (pristine areas of the Tibetan plateau) (Table 2). However, it was noticeable, the concentration of HCHs in Zhongshan Park (ZS) in Xingqing district (74.2 µg/kg) was obviously higher. It perhaps could attribute to the fact that Zhongshan Park has been built up in 1929 and HCHs had been wildly used for protecting garden vegetation from the 1950s to 1980s in China. Referencing to the class I soil standard of the Chinese environmental quality standard for soils (GB15618-1995, 50 µg/kg), HCHs pollution in urban soils (except for ZS) of Yinchuan city may be categorized as being nonexistent. The composition of β-HCH in investigated soils was strongly dominated, which suggested that it was lack of recent HCH sources in comparison with the fraction of β-HCHs in technical HCHs (5%–14%, Li et al. 2006). And the ratio of α-/γ-HCH was relatively stable with a value of 5.0–5.4 for the technical HCH, the ratio for lindane manufactured in China is nearly zero, which can be used as a rough estimation of the source of whether was from technical HCHs or lindane (Kim et al. 2002). The isomer ratio of α-/γ-HCH ranged from 0.168 to 0.963, indicating that the source of HCHs was from mixture with technical HCHs and lindane in the present study.

For DDTs, the levels (equivalent sum of *p,p*′-DDT, *p,p*′-DDE, *o,p*′-DDT and *p,p*′-DDD) varied from 0.577 to 1068 µg/kg with the median of 2.24 µg/kg. The concentrations of ΣDDTs in the most soils were evidently lower than the class I soil standard of the Chinese environmental quality standard for soils (GB15618-1995, 50 µg/kg) and were closed to the concentration of DDTs in background soils in China (pristine areas of the Tibetan plateau)

Table 2 Comparison of the concentrations (μg/kg, dry weight) of HCHs and DDTs in soils

Area	Land use	ΣHCHs	ΣDDTs	Reference
Romania	Rural soil	28.4 ± 33.7	226.9 ± 157.2	Covaci et al. 2001
Romania	Urban soil	29.2 ± 27.1	113.1 ± 151.8	Covaci et al. 2001
Colombia	Rural soil	150	3,119	Finizio et al.1998
Pearl River Delta, China	Rural soil	ND–7.87	ND–176.63	Li et al. 2006
Tibet, China	Undisturbed Soil	0.2–5.4	ND–28.3	Fu et al. 2001
Hong Kong, China	Rural soil	6.19 ± 1.31	0.52 ± 1.01	Zhang et al. 2006
Tianjin, China	Rural and urban soil	45.8	49.6 ± 126.8	Gong et al. 2004
Beijing, China	Park soil	0.2490–197.0, 2.129 (Geometric)	5.942–1,039, 65.64 (Geometric)	Li et al. 2008
Beijing, China	Exurb soil	ND–7.3	ND–76	Wang et al. 2007
Yinchuan, China	Urban soil	0.306–74.2, 0.852 (median)	0.410–1,068, 2.24 (median)	Present study

ND = not detected

(Table 2). It suggested that DDTs pollution in urban soils (except for ZS) could be considered as no pollution. Nevertheless, the concentration of DDTs (1,068 μg/kg)in soils of ZS was significantly much higher than those in other sites in this study, and even exceeded the class III soil standard of the Chinese environmental quality standard for soils (1,000 μg/kg). It was necessary to further study the source of DDTs in ZS for controlling/reducing the exposure of human. Several properties of DDT can be used to infer chemical sources and distinguish fate processes. The ratio p,p'-DDT/(p,p'-DDE + p,p'-DDD)can be used as an indicator of the resident time of p,p'-DDT in the environment. The ratio <1 is generally expected for aged mixtures DDT in environment and a ratio >1 means new input of parent DDT (Qiu et al. 2004). In this study, DDE accounted for comparatively high percentage (32.84–62.86%) and the ratio p,p'-DDT/(p,p'-DDE + p,p'-DDD) <1 was found in all samples, which implied that the residue of DDTs rooted from historical usage rather than new input. Otherwise, the application of dicofol could also introudce DDTs to the environment. And the ratio of o,p'-DDT/p,p'-DDT was used to estimate contamination source which came from technical DDT or technical dicofol (Qiu et al. 2005). Generally, o,p'-DDT/p,p'-DDT ranged from 0.2 to 0.3 in technical DDTs and from 1.3 to 9.3 or higher in dicofol (Qiu et al. 2005). In this study, the ratios were between 0.3 and 1.3, which suggested that both dicofol-type DDT and technical DDT application may be present in the study area.

Besides isomer ratios, EFs of chiral compounds (α-HCH and o,p'-DDT) could be as another feasible approach to provide further information about whether it is being currently applied or residue from past application (Shen et al. 2004; Kurt-Karakus et al. 2005). In this study, both α-HCH and o,p'-DDT in all samples were non-racemic, suggesting the application of historical HCH and DDT (Table 3). This affirmed the judgment above by isomer ratios about the "old" source of HCH and DDT. In addition, it was also found that (+) enantiomers of both α-HCH and o,p'-DDT were preferentially depleted except for BH and G2. This did not agree with the results in Alabama soils (Wiberg et al. 2001) and Pearl river delta soils (Li et al. 2006), which were preferential depletions for (−) enantiomer of chiral α-HCH and o,p'-DDT.

Table 3 EFs of α-HCH and o,p'-DDT in urban soils form Yinchuan city, China

Sample sites	α-HCH	o,p'-DDT
BT	0.373	0.475
ZS	0.252	0.374
BH	0.745	0.521
MC	0.193	0.450
SL	0.409	0.487
YH	0.334	0.431
XX	0.254	0.428
SH	0.338	0.486
G1	0.224	NA
G2	0.473	0.873
F1	0.270	0.0480
F2	0.325	0.444

NA = not available

The study offers the information about the residual levels and chiral signatures of HCHs and DDTs in urban soils of Yinchuan city, China. The results demonstrated that the residual of HCHs and DDTs will have little risk to ecological environment and human health. Combination of isomer ratios and enantiomeric composition analysis, the sources of HCHs and DDTs mainly originated form historical application rather than new input, suggesting the effectively management of Chinese government for restricting the application of HCHs and DDTs. Accordingly, it showed that chiral signature of pollutants was useful in the aspect of tracing the contamination source.

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